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Comparison of the tandem mass spectrometry analysis of compounds of general structure $R_2R'SnPh$, $RR'SnPh_2$ with R_4Sn analogues

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Positive ion-electron impact (EI) mass spectra of some novel organotin compounds have been recorded. These compounds were of the type Me_2SnRR' (where R = Me, Ph and R′ = Ph) and $R_2R'SnPh$ (where R = Me, *n*-Bu, *n*-Pe and R′ = Me, *n*-Bu, *n*-Pe). The spectra were also examined by tandem mass spectrometry (MS–MS) in order to establish fragmentation reaction mechanisms for compounds bearing mixed substituents, particularly the effect of the presence of aryl substituents. In addition, the resultant EI and MS–MS spectra for these compounds were compared with those of R_4Sn (R = Me, Bu, Pe, Ph). The results show that mixed substitution of tetra-alkyl/aryl compounds has a significant effect on the behaviour of these compounds in the mass spectrometer. This effect can be illustrated by examining the fragmentation reaction pathways for the various compounds studied. Fragmentation patterns of nine organotin compounds, based on precursor–product ion relationships are proposed. This technique has the potential to predict the effect of substitution on the mass spectra of organotin compounds and probably organolead and organogermanium compounds.

Keywords: organotin compounds; fragmentation pathways; tandem mass spectrometry; electron impact

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1 INTRODUCTION

One of the first serious attempts to study conventional positive ion-electron impact (EI) mass spectra of organotin compounds of general formula R_3SnR' was reported by Gielen and Mayence.[1] This was followed by a number of other studies,[2,3] which showed a number of common features. Most prominent of these features is the high stability of R_3Sn^+ (for R = Me, Et, Pr, Ph) and/or RSn^+ (for R = Bu) and almost the total absence of any significant molecular ion. Fragmentation pathways for the mass spectra of organotin compounds based mainly on metastable ion data were proposed by Chambers *et al.*[4] Decomposition modes of organotin compounds were explained in terms of the even-bonding- and odd-bonding-electron character of a particular ion on its dissociation reactions.[5] The molecular ions decompose mainly by elimination of odd electron neutral fragments and, therefore, the even-electron ions, R_3Sn^+ and RSn^+, tend to be the most abundant. There is some evidence, in this current work, to suggest the loss of alkene molecules may also lead to ions with increased stability, for example $MeSnPh^{+\cdot}$ [relative abundance (RA) 100%] from $Bu_2MeSnPh$.

Published fragmentation pathways have been collated for those compounds for which metastable ions, tandem mass spectrometry (MS–MS) or some other substantiating evidence is available.[4,5] The speciation of organotin compounds through clear reaction pathways and dissociation modes was made possible by using the technique of MS–MS.[6] The general procedure for this technique, using a triple quadrupole system, involves the selection of a precursor ion(s), which is (are) characteristic of an organometallic compound, using the first mass analyser; each ion is then dissociated by collision with an inert gas in the reaction region. The resultant fragment ions are monitored and detected by scanning the second mass analyser. The MS–MS spectra can be used to construct complete fragmentation pathways[7] by carrying out sequential experiments. Previous studies have shown that the way and extent to which an ion fragments in the reaction region are greatly influenced by the nature and pressure of the gas utilized. Furthermore, the kinetic energy of the selected ions also has an effect

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on the resultant fragmentation. Therefore, when conducting MS–MS experiments it is of paramount importance to ensure consistent analytical conditions, for example fixed primary ion energy and collision gas pressure, in order to obtain reproducible results.

The nature and extent of the substitution has been shown to have a marked effect on the behaviour of organotin compounds in the mass spectrometer.[3,8,9] For example it has been shown[9] that the nature of substituents (aromatic, aliphatic, unsaturated) significantly changes the fragmentation/reaction pathways for compounds of the type R_3SnR', where R′ can be alkyl, aryl, vinyl or allyl. These studies showed that the major fragment ions in the EI mass spectrum of $Bu_3SnVinyl$ are $SnVinyl^+$ and SnH_2Vinyl^+, whereas for $Bu_3SnAllyl$, Bu_3SnPr and Bu_4Sn the major fragment ions occur at *m/z* 177 and 179, corresponding to $BuSn^+$ and $BuSnH_2^+$ respectively. This difference may be explained in terms of the stabilizing effect exerted by the double bond in the vinyl group, which is in close proximity to the Sn—C bond. The possible effect of a double bond alpha to the Sn—C bond on stabilizing the resultant fragment ion was examined by investigating the mass spectrum of Pe_3SnPh.[9] The fragmentation pathway of this compound was found to be similar to that of $Bu_3SnVinyl$.

Perhaps the most dramatic effect on positive ion mass spectra of organotin compounds as a result of substitution can be illustrated by comparing the EI mass spectra of Ph_3SnCl and Me_3SnCl.[3,8] The most abundant ion in the mass spectrum of Ph_3SnCl is at *m/z* 154, which corresponds to Ph_2^+ (i.e. biphenyl), which could form as a result of two phenyl groups undergoing either intramolecular rearrangement or radical reaction to form very stable neutral species. In contrast, the most abundant ion in the mass spectrum of Me_3SnCl can be found at *m/z* 165, corresponding to Me_3Sn^+, and the stability of this ion may be explained by the inductive effect of the methyl groups to the electron-deficient Sn^+ atom.

A series of similar studies can be carried out by changing the nature of the substituent groups, and these include investigating the mass spectra of some novel organotin compounds.

Positive ion mass spectra and the fragmentation pathways of selected organotin compounds with mixed alkyl and/or aryl substituents were investigated to determine whether:

(1) the relative size of different substituents has any effect on the resulting spectra;

Table 1

Me_4Sn	Bu_4Sn	Pe_4Sn	Ph_4Sn
Me_3SnPh		Pe_3SnPh	
Me_2SnPh_2	Bu_2SnPh_2	Pe_2SnPh_2	
$Me_2PeSnPh$	$Bu_2PeSnPh$		
	$Bu_2MeSnPh$		
	$BuPe_2SnPh$		

(2) increased aromatic substitution significantly changes the fragmentation/reaction pathways.

2 EXPERIMENTAL

Authentic samples of organotin compounds listed in Table 1 were available either commercially or were specifically synthesized. Structures, where necessary, were confirmed by high-resolution mass spectrometry and the purity in all cases was better than 95%. Samples were introduced into the mass spectrometer via the direct insertion probe, which was warmed over the temperature range 50–100 °C. Mass spectra were first recorded under conventional EI conditions. The major fragment ions for each compound were identified and subsequently the precursor–product ion scan mode (MS–MS) spectra for each of these ions were also recorded using a VG Trio 3 triple quadrupole mass spectrometer.

The experimental parameters used throughout this investigation were as follows. Standard EI spectra: mass spectrometer, Q1 only operating; scan rate, *m/z* 35–500 in 1 second; resolution, >1100. MS–MS spectra: Q1 set at *m/z* values selected from results of standard EI experiments; Q2 collision gas, argon at 3.2 mTorr; Q3 scanning *m/z*, 20–500 in 1 second resolution, >1100; collision energy, 6 eV.

3 RESULTS

The compounds investigated in this work are detailed in Table 1. Some of the compounds, omitted from Table 1, for example Bu_3SnPh and Ph_3SnR, have either been reported elsewhere[9] or are included in the table in another column, e.g. Ph_2SnBu_2 is entered in the column headed by Bu_4Sn.

The conventional EI mass spectral data for each

compound under investigation are recorded in Table 2. Each fragment ion occurs as a group of peaks as a result of tin isotopes (six major and four minor isotopes). For simplicity reasons the mass spectral fragmentation data are presented in terms of the peaks relating to the principal isotope, namely ^{120}Sn.

Inspection of the data in Table 2 suggests that whilst the loss of an alkyl/aryl substituent group to produce the R_3Sn^+ species is the initial major fragmentation pathway, the subsequent fragmentation reactions appear very dependent on the nature of the substituent present. Chambers *et al.*[4] and Gielen and Juckscharts[8] observed the elimination of a hydrocarbon radical from the molecular ion of alkyl organotin compounds to produce R_3Sn^+ ions of high RA. Similarly, Ostah and Lawson[9] reported the same process for Ph_3SnR' compounds, whereas the alkyl analogues produced RSn^+ ions at 100% RA. Molecules containing alkyl moieties with carbon chains of two or more (i.e. ethyl and above) were observed to produce fragmentation pathways based on the loss of neutral alkene molecules, leading to the formation of the mono- and dihydride ions R_2SnH^+ and $RSnH_2^+$. The same investigation also showed that for compounds of general formula R_3SnR', where R = *n*-butyl or *n*-pentyl, the nature of the dihydride formed depends on R′. For example when R′ = phenyl or vinyl the dihydride is $R'SnH_2^+$ and not $RSnH_2^+$ as in other species, such as $Bu_3SnAllyl$. According to Chambers *et al.*[4] the relative abundance of the hydride ion is related to the number of alkyl–tin bonds present in the molecule. This was attributed to the stabilizing effect exerted by the relatively close double bond in R′ substituents.

The results from the present investigation, particularly the MS–MS data, show that there is no one single fragmentation scheme applicable to the range of compounds investigated, and that there is competition between three possible fragmentation routes depending on the nature and number of substituents present in the molecule. The complexity is typified by considering the compounds in the top row of Table 1, where the fragmentation patterns resulting from each of the chemical groups Me–Sn, Alkyl–Sn and Ph–Sn are different from each other.

3.1 Fragmentation patterns of R_4Sn compounds

From the literature data cited earlier, the base peak for these compounds should be R_3Sn^+, which is observed for R = Me and R = Ph, but for R = *n*-Bu and *n*-Pe this ion has RAs of 71% and 24% respectively. In both these latter cases the dihydride ions are the base peak, with the SnR^+ species of a similar abundance. Each of these compounds will be discussed separately.

3.1.1 Me_4Sn

The conventional fragmentation pattern in Table 2 suggests that the sequential loss of methyl groups is the only viable fragmentation route, but the RAs of $MeSn^+$ and $Me_2Sn^{+\cdot}$ (25% and 22% respectively) do not conform to this pattern. The MS–MS data Fig. 1) show that whilst there is only one route to the formation of Me_3Sn^+ and $Me_2Sn^{+\cdot}$, there are two routes leading to both $MeSn^+$ and $Sn^{+\cdot}$.

3.1.2 Ph_4Sn

The MS–MS investigation of this compound shows that part of the fragmentation pathway (Fig. 2) is exactly analogous to that of Me_4Sn, i.e. the sequential loss of the Ph groups (Ph_3Sn^+ = 100%, $Ph_2Sn^{+\cdot}$ = 11%, $PhSn^+$ = 33%). Differences occur, however, resulting from the apparent rearrangement reactions of Ph_3Sn^+, which facilitates the loss of a neutral benzene molecule or the formation of either the biphenyl or biphenylene ions at *m/z* 154 and 152 respectively.

3.1.3 Bu_4Sn and Pe_4Sn

The data in Table 2 for both these compounds, particularly the presence of ions with Sn–H bonds, shows that fragmentation occurs both by the loss of alkyl and alkene groups. $RSnH^+_2$ ions form the base peak for the pentyl derivative and have 98% RA for the butyl compound. The R_3Sn^+ ion has significantly reduced RA, 71% for Bu_3Sn^+ and only 24% for Pe_3Sn^+. This is explained by the fragmentation scheme (Fig. 3) derived from the MS–MS data, which reveals that the molecular ion fragments by three different routes,[5] two include the loss of alkene molecule(s) and an alkyl radical, and the third involves the loss of an alkyl radical only. The loss of the alkene/alkyl moieties must involve some rearrangement reaction comparable to that exhibited by Ph_3Sn^+, since the overall loss is seen as a single step in the Trio 3 apparatus. The observation of these pathways is limited by the low abundance of the molecular ions for the compounds investigated. Further evidence for rearrangement reactions of the $RSnH_2^+$, R_2SnH^+ and R_3Sn^+, ions is the production of $(CH_3)_2SnH^+$ from these ions, but only when R = pentyl. There is no detectable evidence for the formation of this ion in the butyl

Table 2 List of EI^+ mass spectral data for compounds used in this investigation based on mono- isotopic data from ^{120}Sn species

Me_4Sn	*m/z*	165	135	150	120	180	—	—	—	—	—
(180)	RA (%)	100	25	22	12	2	—	—	—	—	—
	Formula	Me_3Sn^+	$MeSn^+$	Me_2Sn^+	Sn^+	Me_4Sn^+					
Ph_4Sn	*m/z*	351	197	51	154	152	153	272	274	77	—
(428)	RA (%)	100	33	32	26	15	14	12	11	8	—
	Formula	Ph_3Sn^+	$PhSn^+$	$C_4H_3^+$	Ph_2^+	$PhC_6H_4^+$	$PhC_6H_4^+$	$PhSnC_6H_4^+$	Ph_2Sn^+	Ph^+	
Bu_4Sn	*m/z*	177	179	291	121	235	41	120	57	43	149
(348)	RA (%)	100	98	71	63	62	43	30	27	15	8
	Formula	$BuSn^+$	$BuSnH_2^+$	Bu_3Sn^+	SnH^+	Bu_2SnH^+	$C_3H_5^+$	Sn^+	$C_4H_9^+$	$C_3H_7^+$	$C_2H_5Sn^+$
Pe_4Sn	*m/z*	193	191	263	43	57	41	333	121	71	151
(404)	RA (%)	100	86	79	68	64	42	24	22	10	8
	Formula	$PeSnH_2^+$	$PeSn^+$	Pe_2SnH^+	$C_3H_7^+$	$C_4H_9^+$	$C_3H_5^+$	Pe_3Sn^+	SnH^+	$C_5H_{11}^+$	$Et_2SnH_2^+$
Me_3SnPh	*m/z*	227	197	120	135	51	77	212	165	242	—
(242)	RA (%)	100	44	18	16	14	12	11	3	2	—
	Formula	Me_2SnPh^+	$SnPh^+$	Sn^+	$MeSn^+$	$C_4H_3^+$	Ph^+	$MeSnPh^+$	Me_3Sn^+	Me_3SnPh^+	
Me_2SnPh_2	*m/z*	289	197	120	51	227	77	137	135	304	—
(304)	RA (%)	100	25	20	11	9	8	4	3	1	—
	Formula	$MeSnPh_2^+$	$SnPh^+$	Sn^+	$C_4H_3^+$	Me_2SnPh^+	Ph^+	$MeSnH_2^+$	$MeSn^+$	$Me_2SnPh_2^+$	
Pe_3SnPh	*m/z*	197	199	269	43	339	41	57	120	71	—
(410)	RA (%)	100	87	71	70	47	43	11	8	4	—
	Formula	$SnPh^+$	$SnPhH_2^+$	$PeSnPhH^+$	$C_3H_7^+$	Pe_2SnPh^+	$C_3H_5^+$	$C_4H_9^+$	Sn^+	$C_5H_{11}^+$	
$Bu_2PeSnPh$	*m/z*	305	41	325	43	57	197	71	311	235	179
(382)	RA (%)	100	49	47	43	37	30	29	21	7	4
	Formula	Bu_2PeSn^+	$C_3H_5^+$	$BuPeSnPh^+$	$C_3H_7^+$	$C_4H_9^+$	$SnPh^+$	$C_5H_{11}^+$	Bu_2SnPh^+	Bu_2SnH^+	$BuSnH_2^+$
$Bu_2MeSnPh$	*m/z*	213	269	197	135	41	311	120	249	43	—
(326)	RA (%)	100	71	37	29	28	27	17	14	2	—
	Formula	$MeSnPhH^+$	$BuMeSnPh^+$	$SnPh^+$	$MeSn^+$	$C_3H_5^+$	Bu_2SnPh^+	Sn^+	Bu_2MeSn^+	$C_3H_7^+$	
$Me_2PeSnPh$	*m/z*	227	213	197	151	221	283	43	135	41	120
(298)	RA (%)	100	35	33	27	22	21	18	15	15	10
	Formula	Me_2SnPh^+	$MeSnPhH^+$	$SnPh^+$	Me_2SnH^+	Me_2PeSn^+	$MePeSnPh^+$	$C_3H_7^+$	$MeSn^+$	$C_3H_5^+$	Sn^+
$BuPe_2SnPh$	*m/z*	319	339	197	325	43	199	41	269	249	255
(396)	RA (%)	100	43	43	42	36	32	31	24	12	12
	Formula	$BuPe_2Sn^+$	Pe_2SnPh^+	$SnPh^+$	$BuPeSnPh^+$	$C_4H_7^+$	$SnPhH_2^+$	$C_3H_5^+$	$PeSnPhH^+$	$BuPeSnH^+$	$BuSnPhH^+$
Bu_2SnPh_2	*m/z*	275	197	331	43	120	41	311	57	255	77
(388)	RA (%)	100	79	67	35	22	13	9	8	6	5
	Formula	$SnPh_2H^+$	$SnPh^+$	$BuSnPh_2$	$C_3H_7^+$	Sn^+	$C_3H_5^+$	Bu_2SnPh^+	$C_4H_9^+$	$BuSnPhH^+$	Ph^+
Pe_2SnPh_2	*m/z*	345	275	197	43	41	57	120	71	269	339
(416)	RA (%)	100	76	69	54	28	18	14	8	4	3
	Formula	$PeSnPh_2^+$	$SnPh_2H^+$	$SnPh^+$	$C_3H_7^+$	$C_3H_5^+$	$C_4H_9^+$	Sn^+	$C_5H_{11}^+$	$PeSnPhH^+$	Pe_2SnPh^+

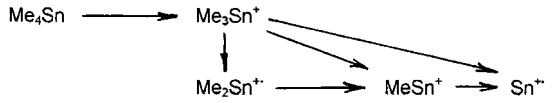


Figure 1 Simplified fragmentation pathway for Me_4Sn.

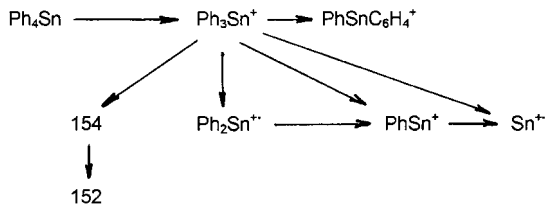


Figure 2 Simplified fragmentation pathway for Ph_4Sn.

compound, nor in compounds containing the Sn—Ph bond. In both compounds there was a significant contribution to the conventional mass spectrum (Table 2) from the fragmentation and charge retention of the alkyl chain substituents (*m*/*z* 57, 43, etc.).

3.2 MS–MS experiments

MS–MS experiments were carried out on compounds with different substituents in order to establish the appropriate reaction pathways. However, it became evident that there was no single general reaction pathway that could be used to represent the MS–MS results for all the tin compounds in question. This is not surprising, owing to the presence of various substituents (Me, *n*-Pe, *n*-Bu, Ph) in different combinations.

The isotope ^{120}Sn was used to elucidate the overall fragmentation patterns, and in some areas the results were confirmed by parallel determinations based on the ^{118}Sn isotope. This was particularly important where the loss of hydrogen atoms was suspected.

For the purposes of the following discussions, compounds with the same fragmentation pathways in the MS–MS analyses have been grouped together. One of the main features of these reactions is the elimination of one or more alkene molecules and the formation of mono-, di- and, in some cases, tri-hydride species, where the compounds include one or more *n*-butyl and/or *n*-pentyl groups. This is in accordance with previous results obtained by other researchers.[4,8] This process is absent when the substituent is the methyl or phenyl group.

3.2.1 Me_2SnRR' compounds

The structures of the major ions in the conventional EI positive mass spectra of these compounds are recorded in Table 2. The compounds Me_2SnPh_2 and Me_3SnPh exhibited fragmentation processes (Fig. 4) that were analogous to those of Me_4Sn. The data in Fig. 4 are a combination of the fragmentation processes exhibited for Me–Sn and Ph–Sn systems. However, it is interesting to note that there is no evidence for the formation of the biphenyl from Me_2SnPh_2.

The main fragmentation process in these compounds occurs via the loss of a methyl group from the molecular ions. This is followed by the sequential loss of alkyl groups, leading ultimately

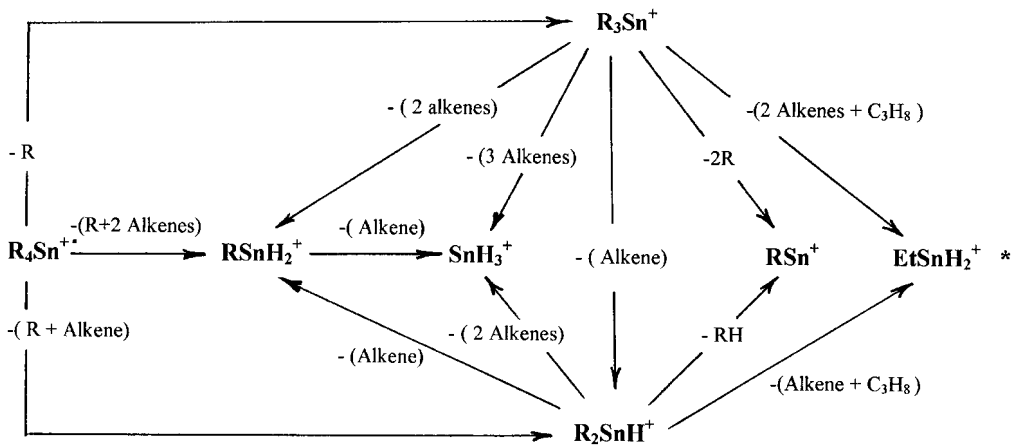


Figure 3 Fragmentation pathway for R_4Sn compounds where R = *n*-Pe or *n*-Bu (*$EtSnH_2$ is not produced where R = *n*-Bu).

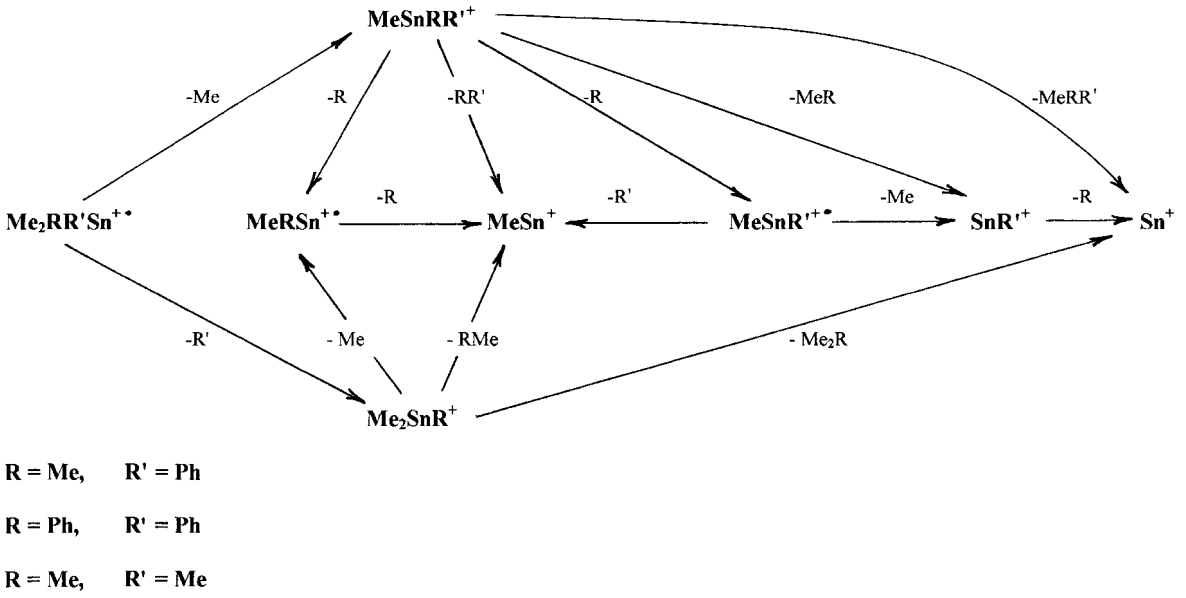


Figure 4 Fragmentation pathways for compounds Me_2SnRR'.

to the formation of the tin ion. $Me_2PeSnPh$ shows the dominant process to be the loss of the pentyl group, followed by the loss of the methyl and other alkyl radicals. $Me_2PeSnPh$ is the only compound in this group that gives the hydride ion Me_2SnH^+, due to the elimination of a pentene molecule. A similar process leads to the formation of $MeSnR'H^+$ in the mass spectrum of the same compound. Furthermore, the SnR'^+ ion is more prominent where R′ = Me or Ph (RA = 16–25%) than in the case where R′ = Pe (RA = 2%).

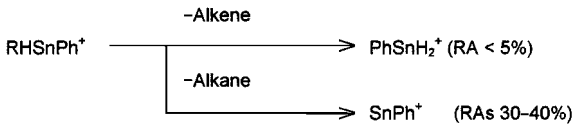
3.2.2 Compounds of general formula $R_2R'SnPh$

The compounds included in this group are: Me_2*n*-PeSnPh, *n*-Bu_2MeSnPh, *n*-Pe_2*n*-BuSnPh and *n*-Bu_2*n*-PeSnPh. The generic fragmentation pathways for these compounds, obtained from the MS–MS studies, are detailed in Fig. 5. As can be seen, the initial fragmentation process is a competitive loss of either the alkyl or the phenyl group to produce the R_2SnPh^+, $RR'SnPh^+$ and $R_2R'Sn^+$ ions. In the general case these ions fragment further by the loss of alkenes, producing mono- and dihydride ions and the ultimate products (not shown in Fig. 5) are $SnH_2^{+\cdot}$ and SnH_3^+. Compounds containing *n*-butyl and *n*-pentyl groups exhibit the significant losses of alkenes, leading to the production of species of the type R_2SnH^+ and $RSnH_2^+$, as well as of relatively high levels of the alkyl fragment ions $C_3H_7^+$, $C_3H_5^+$ and $C_4H_9^+$.

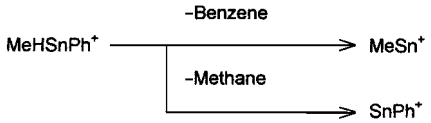
It is interesting to note that whilst this range of compounds has been experimentally shown to follow the same generic fragmentation pattern, the RAs of these ions produced as detailed in Table 2 indicate that the reactions are followed in a competitive manner. Furthermore whilst the major pathways are shown in Figure 5 some minor routes, specific to particular compounds need to be recorded.

3.2.2.1 Fragmentation of $RHSnPh^+$ ions

In the generic scheme (Fig. 5) the fragmentation pathways of this ion include the loss of an alkene or an alkane as shown below:



When R is a methyl group, however, the loss of an alkene is not possible, and two routes involving neutral losses were identified:



Only when R is methyl or phenyl is the species RSn^+ observed at any significant level (RA >5%).

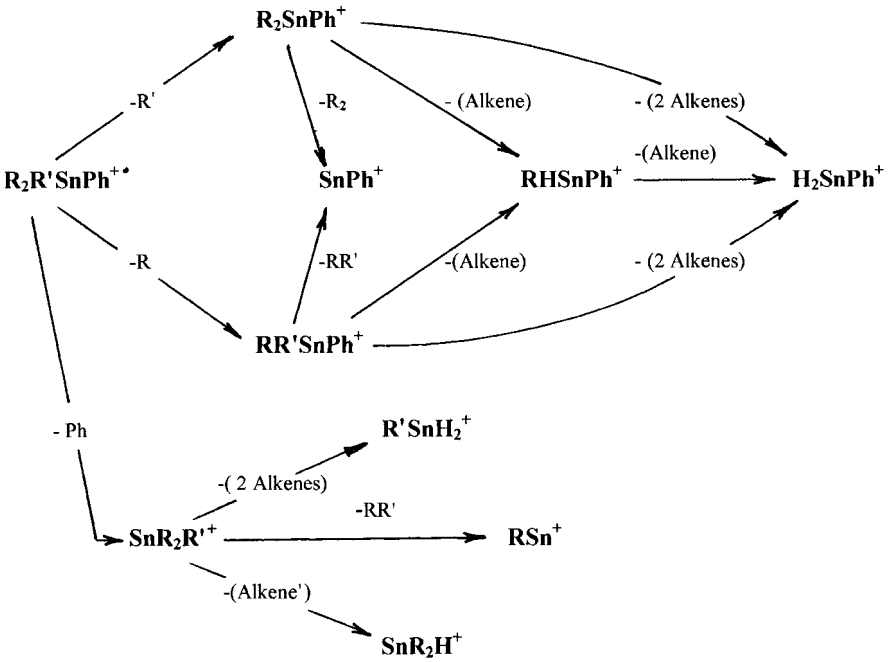
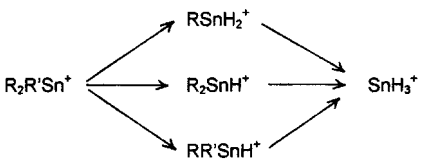


Figure 5 Fragmentation pathways for $R_2R'SnPh$.

3.2.2.2 Compounds containing two or more n*-butyl and/or* n*-pentyl groups*

The generic reaction scheme in Fig. 5 needs to be expanded to cover the fragmentation losses involving several alkene groups. Ions of the type $RR'SnPh^+$ can fragment by alkene losses to produce both $SnPhH_2^+$ and SnH_2^+ ions. Similarly, the $R_2R'Sn^+$ ions can undergo the following routes of fragmentations:



3.3 Compounds of general formula R_2SnPh_2

A generic fragmentation for this group of compounds is shown in Fig. 6. The formation of hydride ions involves the loss of one or more alkene groups. Routes involving the loss of alkene groups have only been observed where there are Bu—Sn or Pe—Sn bonds. From Table 2 it can be seen that as the number of Me—Sn bonds decreases, so the relative abundance of ions containing the Sn—H bond increases. For example for Me_4Sn, $Sn—H^+$ is not detected, for Me_2SnPh_2 the ion $MeSnH_2^+$ (*m*/*z* 137) has an RA of 4% and for $MeBu_2SnPh$ the ion $MeSnPh^+$ (*m*/*z* 213) has an RA of 100%. The conventional EI positive mass spectral data for these compounds, shown in Table 2, is consistent with the pathways identified from the MS–MS experiments.

4 DISCUSSION

The positive ion EI mass spectra of organotin compounds $Alkyl_2SnR'R''$ (where Alkyl is Me, Bu or Pe, R′ = Me, Bu, Pe or Ph and R″ = Me, Bu, Pe or Ph) were dominated by formation of the fragment ion due to the loss of a methyl or butyl group when the alkyl is a methyl or a butyl group respectively. Although the same process occurs when the alkyl is a Pe group, the main fragmentation process is the formation of an SnR''^+ ion (where R″ = Pe or Ph group). Therefore, it is evident that the size of the main alkyl substituent has an effect on the fragmentation of various tin compounds. Furthermore, this is shown by the presence of ions with

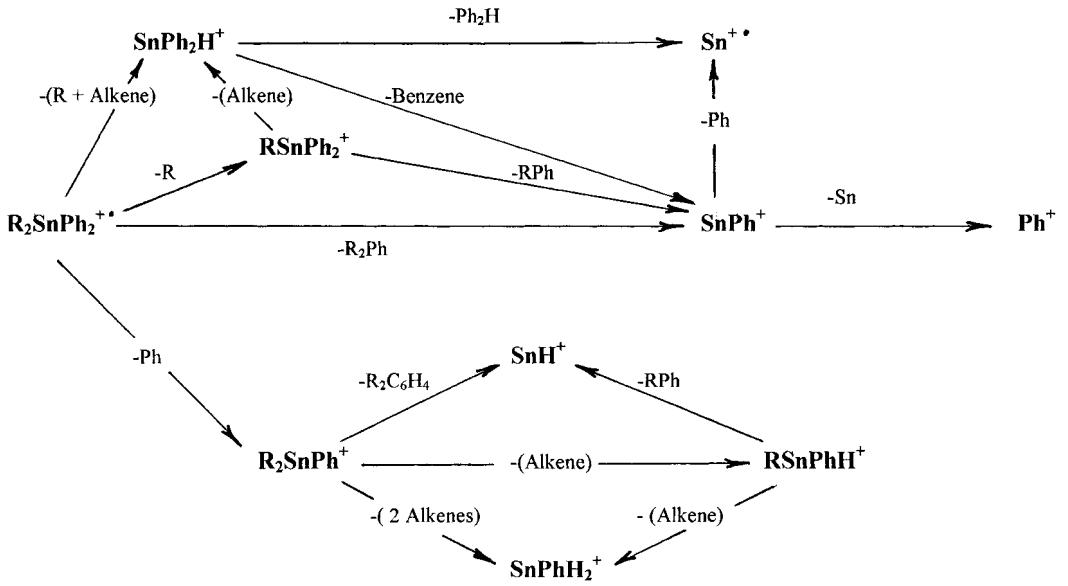


Figure 6 Fragmentation pathways for compounds R_2SnPh_2, where R = Pe or Bu.

relatively high RA values due to fragmentation of the alkyl group itself (*m/z* 41, 43, 57, 71). In this case the Sn—alkyl bonds are no longer equivalent in terms of dissociation energy.

Another feature in the mass spectra of these compounds is the formation of mono- di- and trihydride ions due to the loss of one, two or three alkene molecules respectively. These ions are produced in significant amounts only when the molecule contains two or more butyl and/or pentyl groups in any combination.

In conclusion the mass spectra and fragmentation pathways for organotin compounds are greatly affected by the nature and number of the alkyl and aryl substituents. For example, a methyl group in contrast to a butyl or pentyl group does not go through elimination of an alkene group because of the non-availability of hydrogen atoms on beta and subsequent carbon atoms. The presence of a phenyl group may exert a stabilizing effect on the resultant ion, which contains one or more phenyl groups.

It will be interesting to investigate the relative effect of mixed alkyl substitution on the mass spectra of compounds such as Bu_2SnEt_2, Pe_2SnPr_2, etc.

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